Chemical amplification resists: History and development within IBM

by H. Ito

The chemical amplification concept was invented at IBM Research and quickly brought into use in the production of dynamic random access memory devices in the company. It has remained as an important foundation for the design of advanced resist systems for use in short-wavelength (<300-nm) lithographic technologies.

Introduction

We are perhaps in the most exciting era of microelectronics technology. The home computer market is growing rapidly in quantity and quality. Furthermore, the microlithographic technology, the core technology of semiconductor device manufacture, is drastically changing as the minimum feature size of electronic devices is shrinking to less than 0.25 μm.

Since the resolution (R) is proportional to the exposing wavelength (λ) and inversely proportional to the numerical aperture (NA) of the lens ($R = k\lambda/NA$), higher resolutions are achieved by increasing the numerical aperture or by reducing the exposing wavelength. The most dominant approach to resolution enhancement has been to shift from the G-line (436 nm) to I-line (365 nm) and then to increase the NA of the I-line step-and-repeat exposure tools. Another approach is to move to much shorter wavelengths.

The shift from the near-UV (436–365 nm) to the mid-UV region (300–350 nm) required modification of the diazonaphthoquinone/novolac resist to improve its absorption characteristics at the shorter wavelength [1]. Further reduction of the wavelength to the deep-UV region (254 nm) was sought at IBM in the late 1970s, which necessitated the development of a revolutionary resist system. The classical near-UV positive resist consisting of a novolac resin and a photoactive diazonaphthoquinone dissolution inhibitor does not perform adequately because of its excessive unbleachable (i.e., inability to become more transparent during exposure) absorption in the deep-UV region. Several attempts to overcome the problem were only partially successful [2]. Furthermore, phenolic resins were believed to be too absorbing for use in the deep-UV region, prompting serious research activities to utilize deep-UV-transparent methacrylate polymers in the new lithographic technology [3]. However, low resist sensitivity and poor dry-etch resistance precluded the use of methacrylate resists in semiconductor manufacture. In fact, sensitivity enhancement was a major research subject for many years, but the achievement was only incremental and too marginal to support the new high-resolution technologies. The resist systems based on photochemical events that require several photons to generate one useful product have inherently limited sensitivities.

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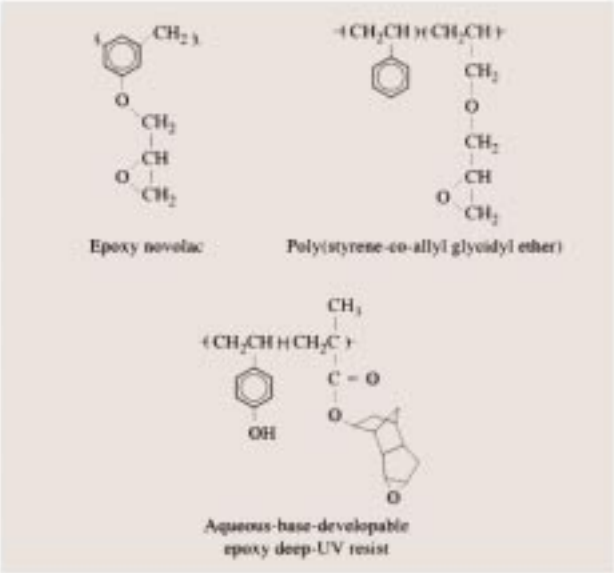
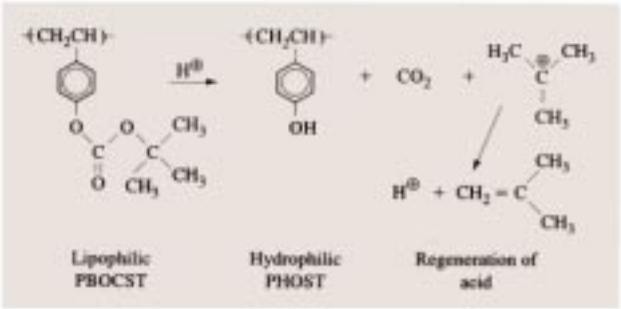


Scheme I

Negative-resist systems based on cross-linking through cationic ring-opening polymerization of pendant epoxy groups.



Scheme II

Acid-catalyzed deprotection for polarity change (tBOC resist); cleavage of a pendant group to convert a lipophilic polymer (PBOCST) to a hydrophilic polymer (PHOST).

Chemical amplification concept

In order to circumvent this intrinsic sensitivity limitation and to dramatically increase the resist sensitivity, the concept of chemical amplification was proposed in 1980 and reported in 1982 [4]. In chemically amplified resist systems, a catalytic species generated by irradiation induces a cascade of subsequent chemical transformations, providing a gain mechanism. The original chemical amplification scheme included

- Cross-linking through ring-opening polymerization of pendant epoxide groups for negative imaging.
- Deprotection (cleavage) of pendant groups to induce a polarity change for dual-tone (positive/negative) imaging.
- Depolymerization for self-developing positive imaging.

These three systems are all acid-catalyzed [4, 5]. The chemical amplification concept[1] was considered as a laboratory curiosity when reported. However, as the value of this totally new system became apparent, it was used in production of 1Mb dynamic random access memory (DRAM) chips by deep-UV lithography in the mid-1980s [6]. Although the use of acid as a catalyst has eventually become the major foundation for the entire family of advanced resist systems, and the semiconductor industry is currently moving steadily toward deep-UV lithography based on chemical amplification resists, IBM already had a long history of DRAM production by deep-UV lithography, made possible by the availability of chemical amplification resists [6, 7] (see the paper by Holmes et al. in this issue [8]).

The above three imaging systems were subsequently refined. The epoxy cross-linking chemistry was developed into the design of high-performance negative resists [9] and also combined with aqueous-base development (**Scheme I**) [10] for semiconductor lithography. However, acid-catalyzed epoxy cross-linking has been most successfully applied to high-aspect-ratio imaging of thick resists [11] (described by Shaw et al. in this issue [12]). The acid-catalyzed depolymerization of polyphthalaldehyde, which was later modified from self-development to thermal development in order to eliminate tool contamination [13, 14], is utilized in all dry bilayer lithography based on thermal development of Si-containing polyphthalaldehyde [14, 15] and also employed in the design of a polymeric dissolution inhibitor [16, 17]. The deprotection mechanism (**Scheme II**) has attracted the most attention and was successfully employed in the manufacture of DRAMs in IBM.

tBOC resist

The diazoquinone/novolac resist was unlikely to be capable of supporting deep-UV lithography. A new base-soluble etch-resistant matrix resin was sought. However, poly(4-hydroxystyrene), or PHOST, commercially available in the early 1980s and employed in a negative deep-UV resist MRS [18], was too absorbing, which gave an incorrect impression that phenolic polymers would not be useful in the deep-UV lithography.

[1] The tBOC resist patent disclosure, which is the basis of all current chemical amplification resists, was initially rated "publish" in the *IBM Technical Disclosure Bulletin*.

The tBOC resist design provided a breakthrough [4, 5, 19]. First of all, this work has demonstrated that "pure" PHOST has a very low absorption in the 250-nm region [20]. PHOST dissolves so fast in aqueous base that the classical dissolution inhibition mechanism is rather incompatible with this phenolic polymer. The problem has been solved by protection of the phenolic OH group with an acid-labile functionality such as *t*-butoxycarbonyl (*t*BOC).

As shown in Scheme II, the IBM tBOC resist consists of poly(4-*t*-butoxycarbonyloxystyrene) (PBOCST), PHOST fully protected with *t*BOC. The lipophilic PBOCST is converted to hydrophilic PHOST by reaction with a photochemically generated acid. This change of the polarity from a nonpolar to a polar state allows dual-tone imaging simply by changing a developer solvent. The use of a polar solvent such as alcohol or aqueous base results in the generation of positive-tone images, while development with a nonpolar organic solvent such as anisole provides negative-tone images. Although this polarity change concept has become the basis for the design of aqueous-base-developable positive-resist systems, the tBOC resist containing triphenylsulfonium hexafluoroantimonate was used in its negative mode in manufacture of 1Mb DRAMs on Perkin-Elmer Micralign® 500 mirror projection scanners operating in the deep-UV mode (**Figure 1**) [6]. This internal availability of sensitive resist systems based on chemical amplification motivated IBM to further deep-UV lithography by developing new exposure tools (Micrascan®) with Perkin-Elmer and then with Silicon Valley Group Lithography. Positive imaging of the tBOC resist was very problematic because of skin or postexposure bake (PEB) delay phenomena [21].

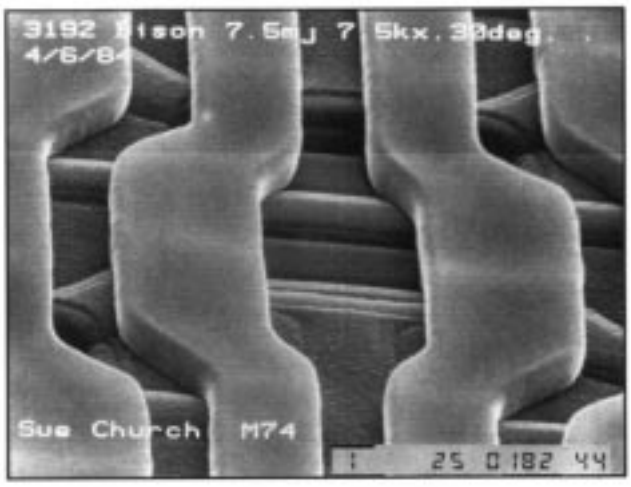


Figure 1

Negative 1-μm images delineated in the tBOC resist on topography by deep-UV mirror-projection printing with a Perkin-Elmer Micralign 500 for 1Mb DRAM production.

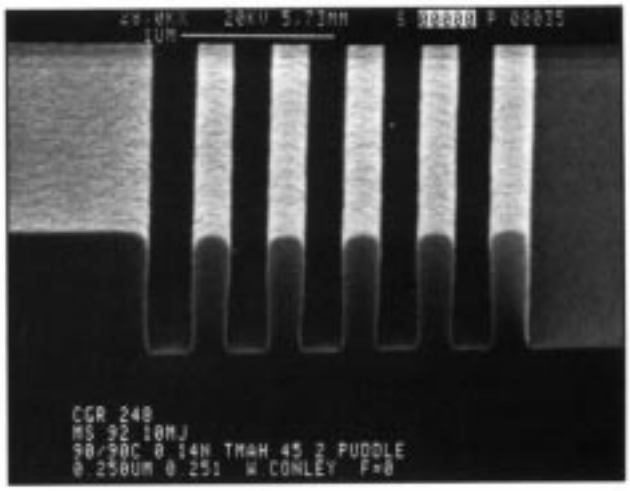


Figure 2

Negative 0.25-μm line/space patterns printed in the CGR resist on Micrascan II (0.50 NA) and by aqueous-base development (courtesy of W. Conley, IBM Microelectronics Division).

Chemically amplified resist family

The use of acid as a catalyst provides design versatility. Varieties of new imaging mechanisms based on acid catalysis and new acid generators for use with chemical amplification resists have been reported [22–24]. The chemical amplification resists can be classified most conveniently according to their imaging mechanisms:

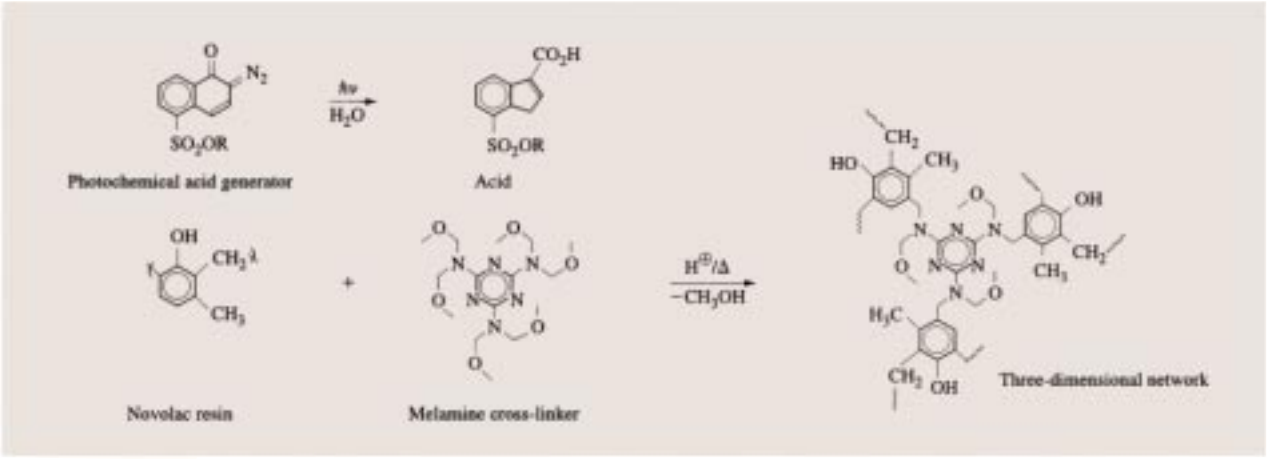
- Deprotection.
- Depolymerization.
- Rearrangement.
- Intramolecular dehydration.
- Condensation.
- Cationic polymerization.

Among the imaging mechanisms listed above, the deprotection (Scheme II) and condensation (**Scheme III**) systems have been studied most extensively by many research groups [22–24], especially for the design of aqueous-base-developable positive and negative resists, respectively. In addition to the intended sensitivity enhancement, the chemically amplified imaging mechanisms provide high contrasts and high resolutions, which have played a decisive role in acceptance of the totally new imaging materials.

Negative resists

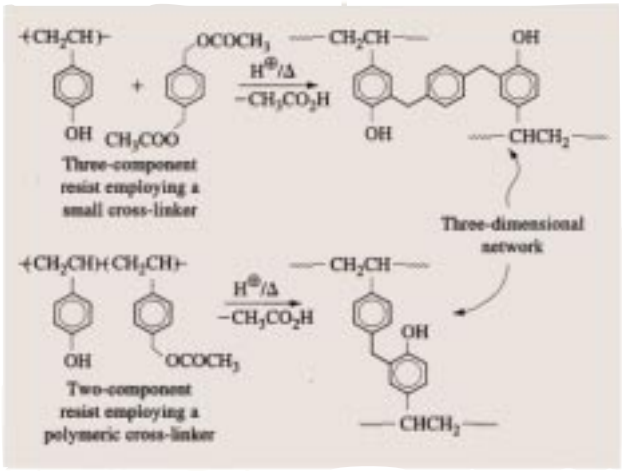
The first commercial chemical amplification resist was a three-component negative system consisting of a novolac

VOL. 41, NO. 1/2, 1997, REPRINT



Scheme III

Cross-linking of a novolac resin through acid-catalyzed condensation with a melamine for negative aqueous-base development.



Scheme IV

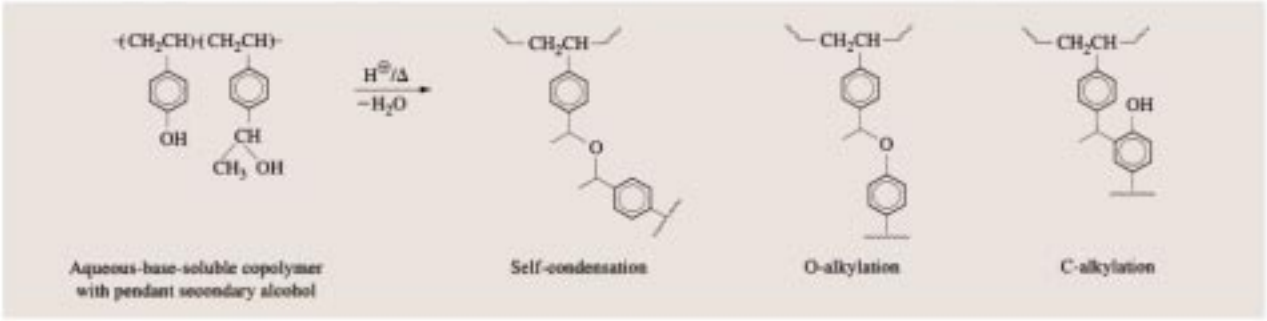
Three-component and two-component negative-resist systems based on cross-linking of PHOST through acid-catalyzed electrophilic aromatic substitution.

resin, a photochemical acid generator, and a melamine cross-linker which undergoes acid-catalyzed condensation with the phenolic resin (Scheme III) [25]. This commercialization allowed the lithographic community to experience the high-resolution capability of chemical amplification resists and promoted further interest in the new imaging concept. The acid-catalyzed condensation involving a phenolic resin is the most dominant imaging mechanism for advanced negative resist systems today [26, 27]. A three-component negative CGR resist based on acid-catalyzed condensation for deep-UV lithography [26] has been developed at IBM and is now marketed through the IBM/Shipley Deep-UV Resist Alliance. Aqueous-base-developed 0.25-μm line/space patterns produced in the CGR resist on a Micrascan II (NA = 0.50) are shown in **Figure 2**. In addition to the three-component design, two-component negative resists based on hydroxystyrene (HOST) copolymers and an acid generator (**Scheme IV**) were extensively investigated [27].

In the above negative-imaging systems, the base-solubilizing electron-rich phenolic group functions as the reaction site (C- or O-alkylation). Aqueous-base-developable negative-resist systems were also formulated utilizing acid-catalyzed intermolecular dehydration of pendant *secondary* alcohol (**Scheme V**) [28].

Negative-resist systems that do not involve cross-linking have been extensively developed at IBM. The first example of such resist systems was the tBOC resist mentioned earlier. The polarity change from a nonpolar to a polar state induced by acid-catalyzed deprotection of the tBOC resist allows swelling-free negative imaging with a nonpolar organic solvent. The concept has been extended to a reverse polarity change from a polar to a nonpolar state in the design of negative systems which can be developed with a polar solvent such as alcohol or aqueous base [28–30]. The chemistries employed to induce the reverse polarity change were acid-catalyzed intramolecular dehydration and pinacol rearrangement (**Schemes VI** and **VII**) [28–30].

Intramolecular dehydration of pendant *tertiary* alcohol converts a hydrophilic functionality to a lipophilic olefin, allowing negative imaging with alcohol as a developer. Similarly, the pinacol rearrangement, which involves acid-



Scheme V

Negative-resist systems based on acid-catalyzed intermolecular dehydration which induces cross-linking through C- and O-alkylation.

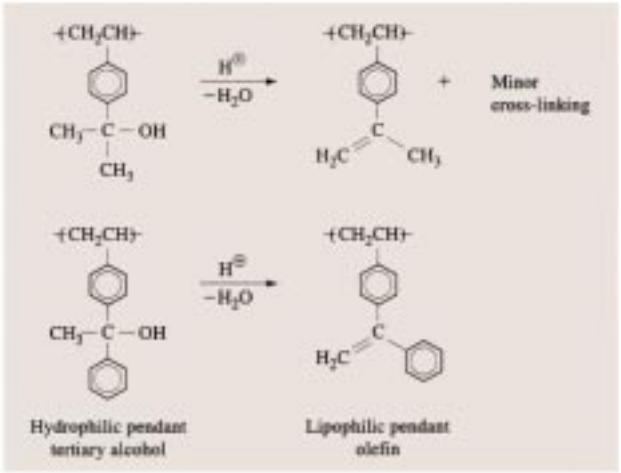
catalyzed dehydration, of *vic*-diol results in the transformation of polar alcohol to less polar ketone or aldehyde, providing a negative system that can be developed with alcohol. Aqueous-base development has been achieved by synthesizing HOST copolymers containing pendant *vic*-diol [28] and also by blending a small *vic*-diol with a phenolic matrix resin [29]. The latter system functions on the basis of conversion of hydrophilic alcohol to dissolution-inhibiting ketone through pinacol rearrangement.

Positive resists

As mentioned earlier, the chemical amplification concept based on photochemically induced acid catalysis has had a significant impact on the design of positive resists. In fact, all modern advanced positive resists are based on acid-catalyzed deprotection of partially protected PHOST (**Scheme VIII**) [4, 5, 19].

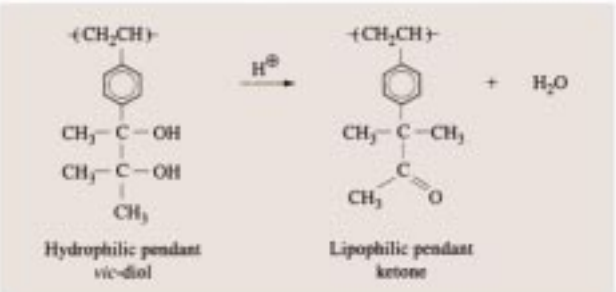
The representative example is the APEX resist [31]. This resist was employed in the manufacture of 16Mb DRAMs, and is currently marketed through the IBM/Shipley Deep-UV Resist Alliance.

The acid-catalyzed deprotection mechanism, which is the foundation for high-contrast positive resists, has allowed the semiconductor industry to extend photolithography to the deep-UV region for higher resolution. However, a major problem recognized in the early 1980s that is particular to chemical amplification resists has appeared: Positive images exhibit T-top (T-shaped profile) or skin formation upon standing after coating, especially after exposure (**Figure 3**) [21]. After numerous attempts to identify the cause, IBM researchers, by using activated carbon filtration [21] and a ^{14}C labeling technique [32] (**Figure 4**), have successfully ascribed the formation of a surface insoluble layer to contamination by a trace amount (of the order of 10 ppb) of airborne basic substances such as *N*-methylpyrolidone (NMP) absorbed



Scheme VI

Acid-catalyzed intramolecular dehydration for polarity change; conversion of hydrophilic pendant alcohol to lipophilic pendant olefin.



Scheme VII

Pinacol rearrangement for polarity change; conversion of polar pendant diol to nonpolar pendant ketone.

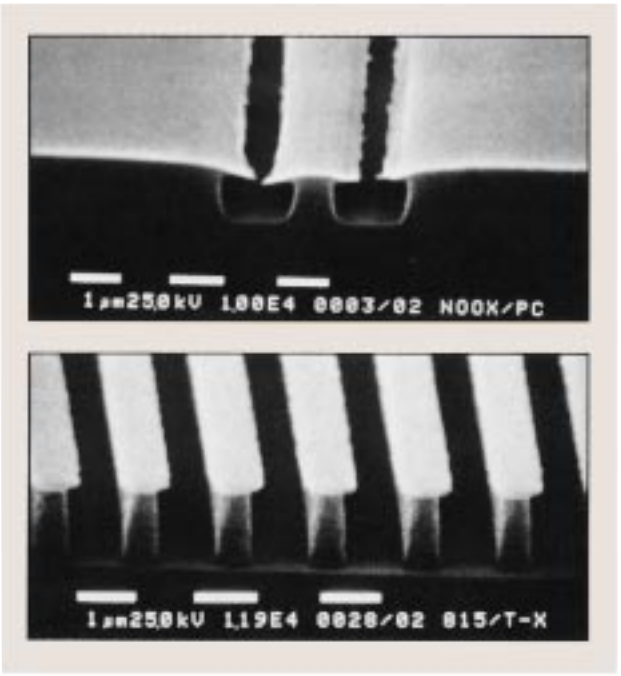


Figure 3

Skin and T-top formation observed in chemical amplification positive resists.

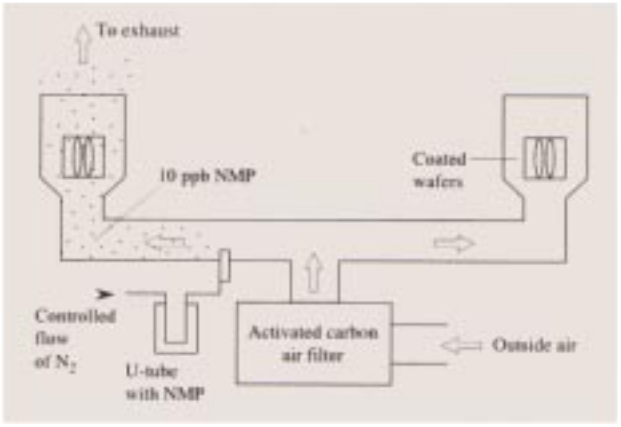
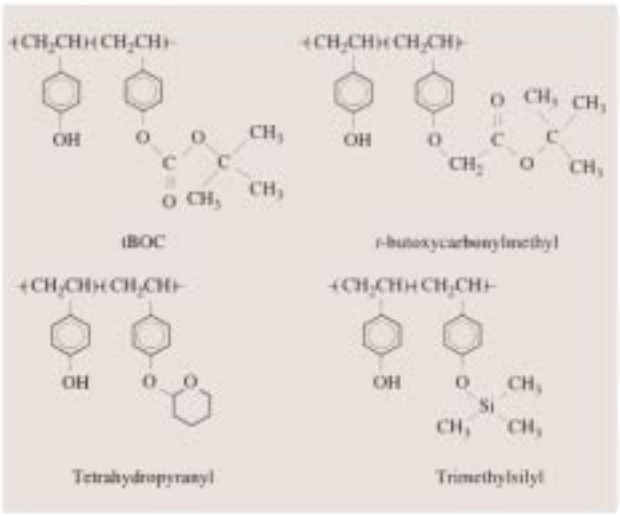


Figure 4

Activated carbon air filtration to protect coated wafers from airborne base contamination, to study absorption of contaminants into polymer films, and to study the effect of a minute but controlled amount of base on lithographic imaging.



Scheme VIII

Aqueous-base-developable positive-resist resins (partially protected PHOST); dissolution-inhibiting pendant protecting group converted to aqueous-base-soluble phenol or carboxylic acid by reaction with a photochemically generated acid.

by the resist film [21]. Because of the catalytic nature of the imaging mechanisms, a trace amount of airborne basic substances absorbed by the resist film interferes with the desired acid-catalyzed reaction. This contamination study was later extended to many other airborne bases originating from, for example, wall paints [21].

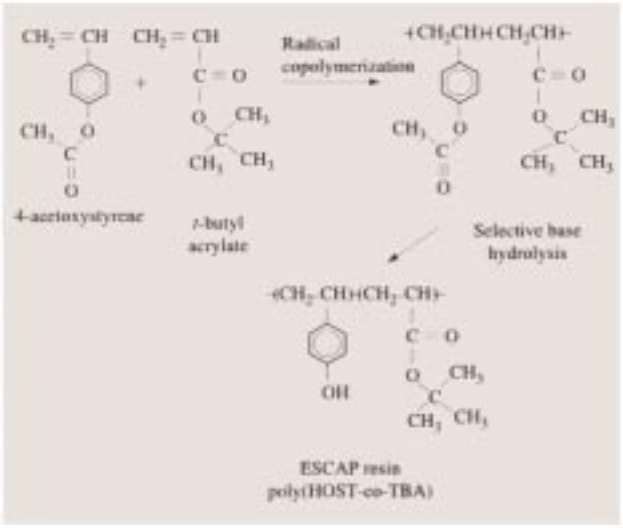
This finding was very pivotal in solving the delay problem of chemical amplification resists. In fact, the activated carbon filtration to purify the enclosing atmosphere has been installed in IBM ever since 1Mb DRAMs were manufactured using the negative tBOC resist [6]. Air filtration to remove airborne bases is now becoming a standard practice in the industry.

Alleviation of the delay problem has been sought, and some engineering solutions have been employed at IBM:

- Purification of the enclosing atmosphere by activated carbon filtration [21].
- Application of a protective overcoat [33–35].
- Incorporation of additives in resist formulation [36, 37].

Two important and more fundamental approaches to the contamination problem have recently been proposed: reduction of the activation energy of deprotection [38] and reduction of the free volume by annealing [39–41]. In the first case, the acid-catalyzed reaction occurs spontaneously at room temperature (without PEB) upon generation of acid by irradiation, while the majority of the chemical amplification resists require PEB and therefore are susceptible to the PEB delay problem.

The annealing concept [42] for environmental stabilization of chemical amplification resists is based on a



Scheme IX

ESCAP resist resin synthesis by radical copolymerization of 4-acetoxystyrene with *t*-butyl acrylate followed by selective base hydrolysis of the acetoxy group.

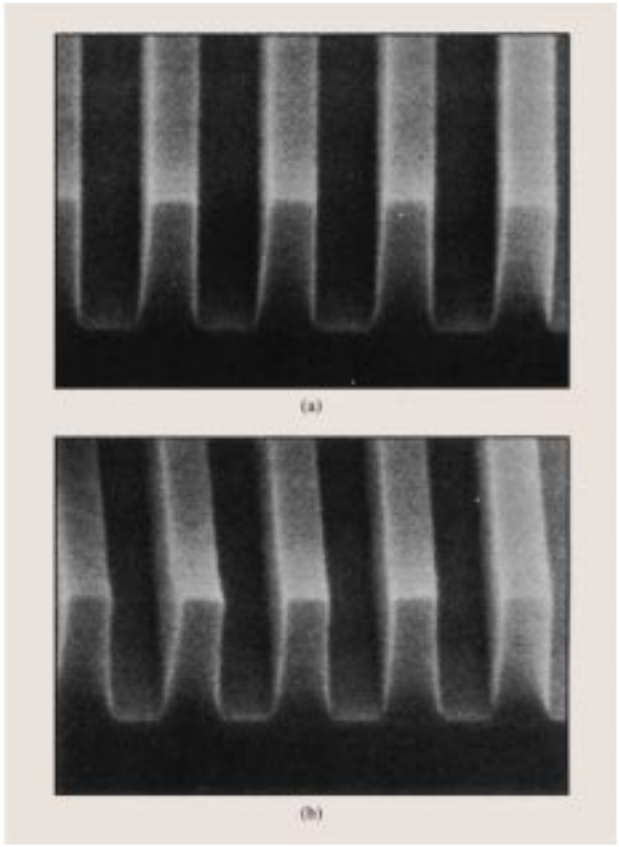


Figure 5

Overnight PEB delay stability of the ESCAP resist 0.35-μm line/space patterns printed on a Micrascan II (0.05 NA) and developed with 0.255 N TMAH: (a) No delay; (b) 18-hr delay.

systematic study on the propensity of thin polymer films to absorb NMP [43]. Polymer films with lower glass transition temperatures (T_g) absorb smaller amounts of NMP because of better annealing and reduced free volume. The validity of the annealing concept has been proven by lowering the T_g of the tBOC-related resist resins through use of *meta*-isomers [39, 40]. Since the diffusivity of small molecules in polymer films is an exponential function of the free volume, a small difference in the free volume is translated to an extremely large difference in the diffusivity.

A production-worthy environmentally stable chemically amplified positive (ESCAP) resist has been designed on the basis of the annealing concept, with its contamination resistance achieved by carrying out the bake processes at unconventionally high temperatures [41, 44, 45]. The resist consists of a copolymer of HOST with *t*-butyl acrylate (**Scheme IX**) and is characterized by its exceptional thermal stability, permitting the film to be baked at temperatures higher than its high T_g of 150°C. Other chemically amplified positive-resist films (Scheme VIII) cannot be annealed because premature thermal deprotection occurs at temperatures below their T_g. ESCAP has demonstrated a superb PEB delay stability in comparison with APEX. **Figure 5** demonstrates the ESCAP overnight delay stability of 0.35-μm line/space patterns exposed on a Micrascan II and developed with 0.255 N tetramethylammonium hydroxide (TMAH) aqueous solution. ESCAP has been selected for commercialization for 256Mb DRAM production by 0.25-μm imaging through the IBM/Shipley Deep-UV Resist Alliance, which has refined the resist to exhibit extraordinary resolution (200 nm on 0.53 NA at 248 nm) (**Figure 6**).

Another important advance in the design of positive chemical amplification resists is their extension to the ArF excimer laser wavelength at 193 nm, which is expected to play a key role in manufacture of 1Gb devices. Although the chemistry of 193-nm lithography is likely to be based on chemical amplification schemes such as acid-catalyzed deprotection which are already available, there are many materials challenges. PHOST cannot be used to formulate single-layer 193-nm resists because of its excessive absorption. Polymethacrylates are highly transparent at 193 nm and are thus used in the design of ArF excimer laser positive resists, with their aqueous-base development achieved by acid-catalyzed conversion of *t*-butyl ester (*t*-butyl methacrylate) to carboxylic acid (methacrylic acid)

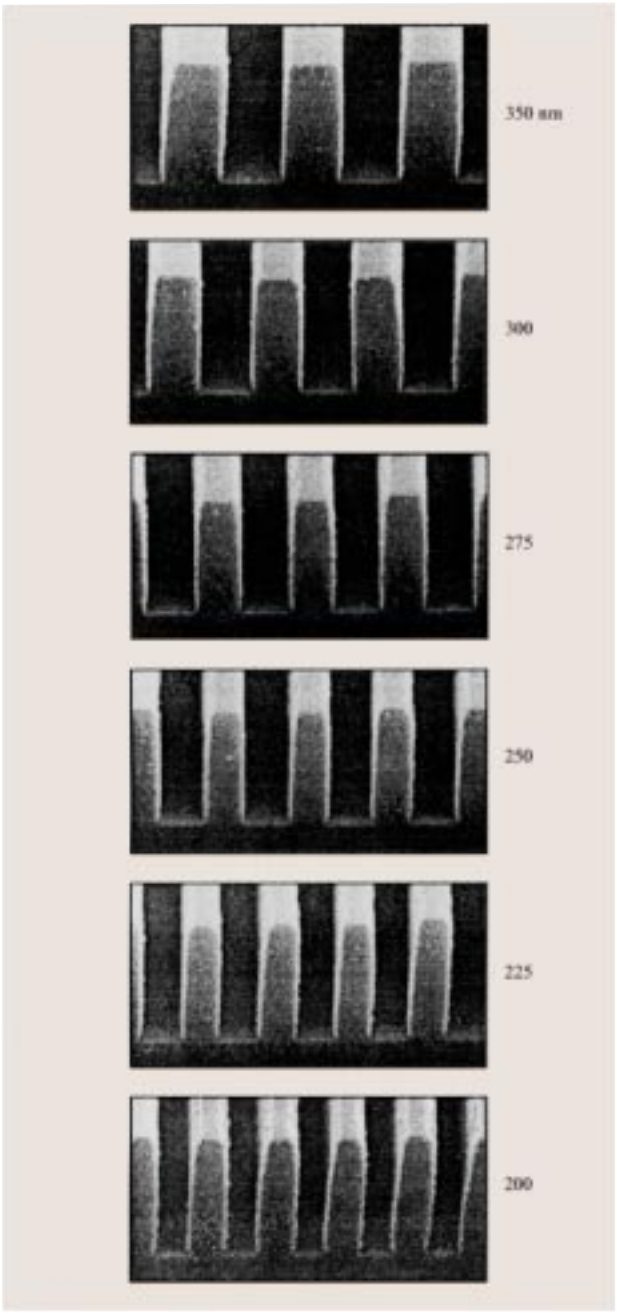


Figure 6

ESCAP linear resolution from 350 nm down to 200 nm on a GCA KrF excimer laser stepper (0.53 NA) (courtesy of Shipley Company).

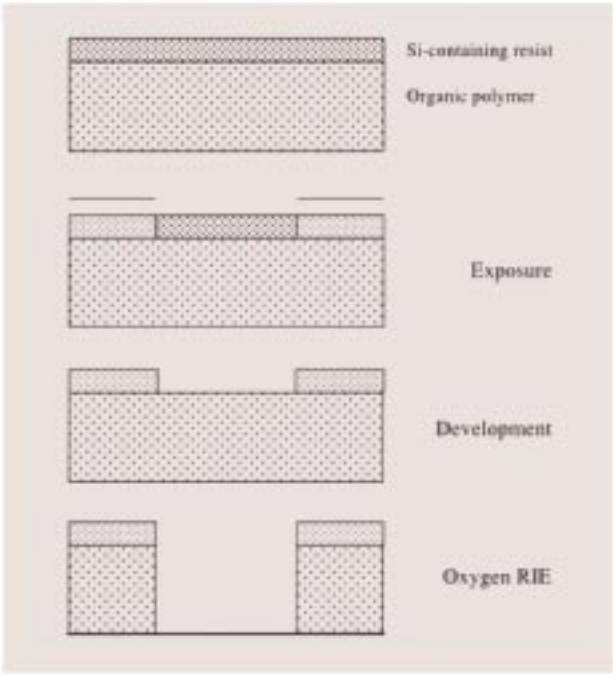
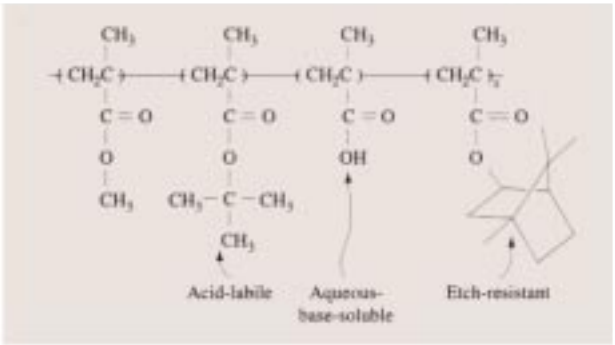


Figure 7

Bilayer lithographic process with a Si-containing resist; the top resist is exposed and developed in a standard fashion and used as a protective mask to etch a planarizing organic polymer bottom layer with oxygen RIE.



Scheme X

Polymethacrylates for ArF excimer laser lithography.

[46, 47]. The IBM resist, a terpolymer of *t*-butyl methacrylate, methacrylic acid, and methyl methacrylate (x = 0, **Scheme X**) was first developed for dry-film laser direct writing [48], but has subsequently been found to function as a high-resolution single-layer positive resist at 193 nm. Since the polymer lacks dry-etch resistance, the resist has been used primarily to qualify prototype ArF excimer laser steppers.

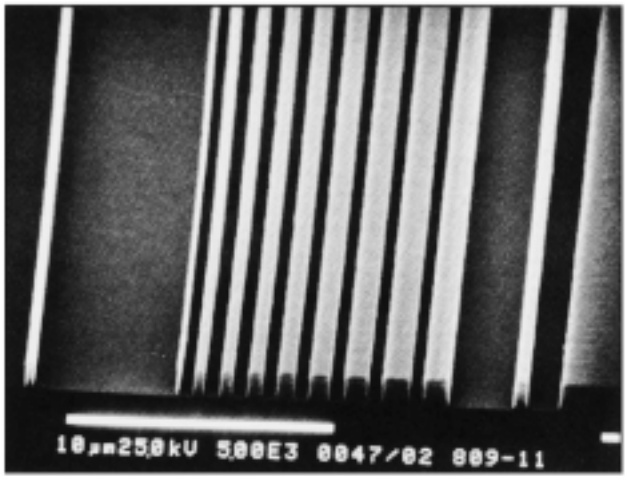
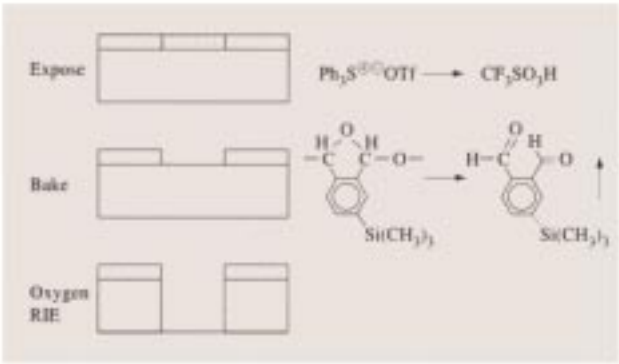


Figure 8

Positive sub-0.5-μm bilayer images delineated by thermal development of poly(4-trimethylsilylphthalaldehyde) followed by O_2 RIE.



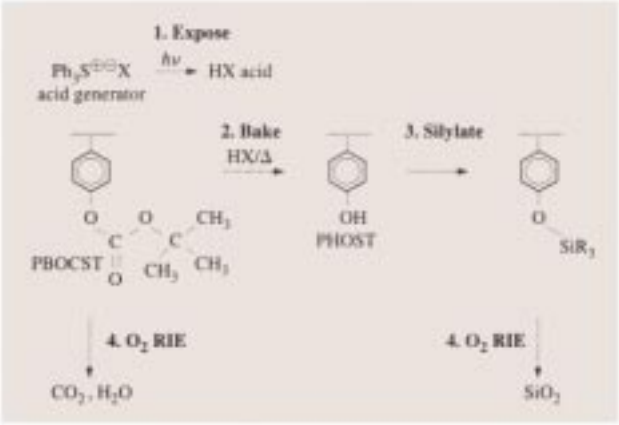
Scheme XI

All-dry bilayer lithography involving thermal development of Si-containing polyphthalaldehyde through acid-catalyzed depolymerization to volatile species followed by O_2 RIE pattern transfer with the developed resist film as a protective mask.

Incorporation of alicyclic structures such as adamantane and norbornane has been shown to enhance dry-etch resistance [47, 49–52]. IBM has employed isobornyl methacrylate as an etch-resistant component (Scheme X) and utilized a dissolution-inhibiting steroid to further increase etch durability [50]. IBM's 193-nm-resist activities are described in detail by Allen et al. in this issue [53].

Bilayer resist systems

The bilayer lithographic scheme utilizing silicon-containing resists was first reported in 1983 by IBM [54] and studied



Scheme XII

Negative dry development based on silylation of PHOST generated in the exposed region through acid-catalyzed deprotection of PBOCST.

extensively by many research groups until a few years ago (**Figure 7**). Although the single-layer technology is favored, the 1Gb generation demands consideration of all alternative technologies including the bilayer scheme. The chemical amplification concept has also been applied to the bilayer lithography based on the use of silicon-containing resists and oxygen reactive ion etching (RIE) for pattern transfer.

Aqueous-base-soluble polysilsesquioxane was protected with the *t*-BOC group to formulate a positive resist based on acid-catalyzed deprotection [55]. Wet development with an aqueous base followed by O_2 RIE pattern transfer results in the generation of high-aspect-ratio images.

A drawback of bilayer lithography is its need for extra processing steps. In an attempt to simplify bilayer imaging, an all-dry process was proposed; it is based on thermal development of poly(4-trimethylsilylphthalaldehyde) through acid-catalyzed depolymerization followed by an O_2 RIE pattern transfer to the underlying layer (**Scheme XI**, **Figure 8**) [14, 15].

All-dry lithographic processes

All-dry lithography has been another important area based on selective silylation of organic resists and subsequent O_2 RIE development, which is a single-layer process that may play an important role in the generation of 1Gb chips.

The deprotection chemistry is uniquely suited to the silylation process. The reactive phenolic functionality unmasked by acid-catalyzed deprotection is selectively and covalently reacted with a gaseous silylating agent such as hexamethyldisilazane. This renders the exposed region impervious to O_2 plasma, while the organic polymer film in the unexposed regions is rapidly etched by O_2 RIE (**Scheme XII**) [56, 57]. This process provides negative-tone

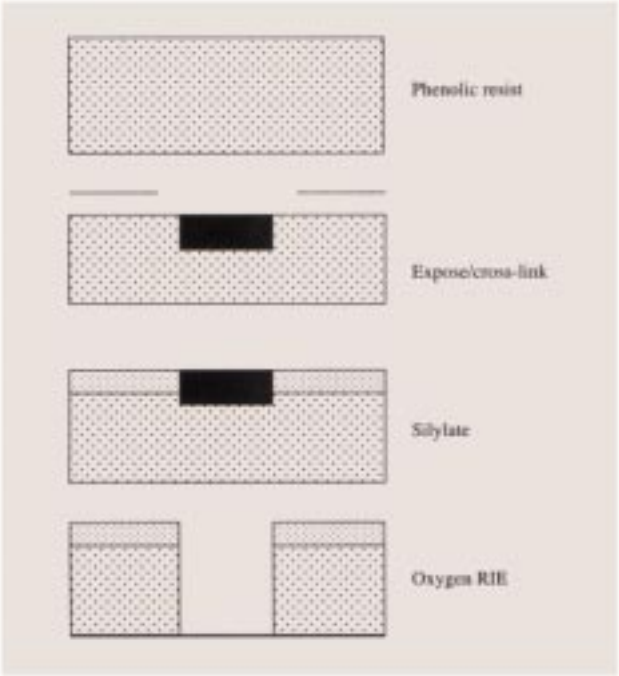


Figure 9

Positive dry development based on diffusion-controlled selective silylation of cross-linking phenolic resists; a silylating reagent reacts with an unexposed phenolic resist but does not diffuse as much into the exposed/cross-linked area.

images, and the silylation selectivity is based on the high-contrast reactivity difference.

An alternative silylation process first reported by UCB [58] is based on diffusion-controlled silylation of diazonaphthoquinone/novolac resists; thermally cross-linked unexposed areas are less susceptible to silylation because of limited diffusion, while the un-cross-linked novolac resin in the exposed region is silylated. This silylation technique of cross-linking phenolic resists has been successfully applied to chemical amplification resists based on acid-catalyzed condensation, which provide positive images upon O_2 RIE (**Figure 9**) [59].

Summary

The chemical amplification concept was invented by IBM and quickly applied to the manufacture of DRAMs by deep-UV lithography. After more than fifteen years since its invention, the entire lithography community is moving toward deep-UV lithography, a technology made possible by chemical amplification. In addition to enhanced sensitivity, high contrast and high resolution are the major reasons for the industry-wide acceptance of chemical amplification. Materials and processes of chemical amplification resists will continue to be refined to support highly demanding future lithographic technologies.

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Received February 9, 1996; accepted for publication October 31, 1996

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